学位論文要旨

Thermoluminescence characteristics of calcite for precise age determination

方解石の熱ルミネッセンス特性研究と正確な年代測定への応用

金沢大学自然科学研究科
自然システム学専攻

学籍番号: 1424062004
氏　名: 小形学

Abstract

Thermoluminescence dating method has been applied to calcite, but it is less popular partly because the difference in luminescence response for different kinds of radiation is not clear. To report more reliable thermoluminescence ages for calcite, fundamental characteristics of its response to radiation exposure were investigated and related to chemical composition by analyzing natural and synthetic calcites with controlled impurity concentrations. Relative thermoluminescence efficiencies by beta or gamma irradiations for calcite against quartz are under 1.0, and it indicates that equivalent dose of calcite samples were underestimated when calibration curve was created with X-ray source calibrated using quartz. This may be caused by differences in common substitution elements in calcite versus quartz. Thermoluminescence efficiency by gamma ray is inversely proportional to logarithm of Mg+Mn+Fe concentrations. Thermoluminescence efficiency by beta ray must be considered together with the cathodoluminescence emission. Fe may prevent release of beta radiation energy as a form of cathodoluminescence and increase the thermoluminescence efficiency. Finally, calcite thermoluminescence dating was applied to understand the timescale necessary for bentonite–alkaline groundwater reaction in a geological framework. A deep geological repository for radioactive waste from nuclear reactors is composed of several barriers including bentonite, thus the stability of the bentonite during the interaction with the alkaline groundwater is an important issue. Provided appropriate corrections in annual dose considering impurity concentrations, the time scale was estimated as more than 100kyrs.

Calcite is a ubiquitous mineral found in many geological formations, thus calcite is useful to provide information for geological and archaeological age determination (Wefer and Berger, 1991, Suzuki et al., 1999, Flotté et al., 2001, Roque et al., 2001, Watanabe et al., 2008, Kano, 2012). ^{14}C and Th/U disequilibrium dating have been applied to calcite (Plagnes et al., 2003); however, applicable ages from these dating methods are up to 5×10^4 (^{14}C) and 5×10^5 (Th/U) years. Furthermore, Th/U dating is difficult to apply to samples contaminated with detrital thorium (Debenham and Aitken, 1984).

When dielectric minerals interact with ionizing radiation, semi-stable electron and hole trapping sites are created within forbidden band. These minerals emit luminescence when heated and this phenomenon is referred to as thermoluminescence (TL). The emitted luminescence intensity is proportional to the accumulated radiation dose applied to the mineral by environmental radioisotopes. Therefore, TL can be applied to the dating of archaeological artifacts, volcanic products and sediments (Aitken, 1985). Quartz, feldspar and calcite are known to be TL emitters in the geoscience field. The advantages of TL dating are (1) a dating limit of up to 10^6 years ago, which is longer than ^{14}C and Th/U, (2) radioelements are not necessary to be present in the target mineral, so it is applicable to a variety of minerals, and (3) age information is reset by heating and thus can record thermal events. TL emitted from calcite has been used to date many types of events (Franklin et al., 1988, Debenham and Aitken, 1984, Roque et al., 2001).

In comparison to quartz TL, characteristics of calcite TL are less understood, thus TL dating was not often applied to calcite in recent years. Earlier studies suggested that characteristics of TL depend on impurity concentrations (Medlin, 1959, Townsend et al., 1994), however, it is not quantitatively understood and the difference in characteristics of luminescence response against different kinds of radiation is not clear. In this study, we investigate the relationship between impurity concentration and calcite TL efficiency by each radiation.

The color of the emitted TL varies among different samples, thus the determination of detection wavelength is important for luminescence measurement. The author created and improved a java application to handle RGB (red-green-blue) information of thermoluminescence color images (TLCI) obtained using a digital camera (Chapter 1). This Java application is able to numerically treat TLCI of various image size and resolutions, and visually represent TL color on a CIE (Commission Internationale de I'Eclairase) chromaticity diagram (Fig. 1).

In chapter 2, the author evaluated the relationship between impurity concentration and TL efficiency induced by each radiation using natural calcites. A known dose of beta, gamma or alpha radiation were introduced to calcite samples, which were then measured by the single aliquot regenerative dose (SAR) method (Murray and Wintle, 2000) using X-rays, which is calibrated using quartz, as an external artificial source. Relative TL efficiencies for calcite by beta, gamma or alpha irradiation against quartz (hereafter called beta, gamma and alpha efficiency, respectively) were calculated as [measured dose/given dose]. Beta and gamma efficiencies are 0.19-0.34 and 0.16-0.33, respectively, and it indicates that equivalent dose of calcites samples were underestimated when calibration curve was created with X-ray source calibrated using quartz. This may be caused by differences in common substitution elements in calcite (^{20}Ca, ^{25}Mn and ^{26}Fe) versus quartz (^{3}Li, ^{11}Na, ^{13}Al and ^{14}Si). Interaction between mediums and radiation is affected by radiation energies more sensitively for calcite than quartz (Davisson and Evans, 1952). The gamma efficiency may depend on the Mn concentration; however, it is not clear which elements affect the beta efficiency (Fig. 2) due to complex impurity concentration of natural calcites. The accumulated dose from alpha rays is affected by sample thickness because of the spatial energy density around the center of the alpha track and the instrumental luminescence detection range. Thus, for accurate alpha efficiency measurements, evaluation of the effective alpha ray range and instrumental luminescence detection thickness is important. The k-value (alpha efficiency against gamma efficiency) increases with Mn concentrations (Fig. 3). Zimmerman (1972) suggested that the alpha efficiency is lower than beta and gamma efficiency because the ionization density produced by alpha particles is so great that the TL traps in the central core of tracks become saturated. This leads to a much greater proportion of the ionized electrons going to waste than with beta and gamma radiation. Thus, the author concluded that luminescence traps increase with increasing Mn concentrations.

In chapter 3, synthetic calcites with controlled impurity concentrations were analyzed to evaluate relationship between multiple impurity concentration and beta or gamma efficiencies. Samples were doped with Mg, Mn and Fe. Gamma and beta efficiencies of synthetic samples are 0.115-0.398 and 0.122-0.481, respectively. The gamma and beta efficiencies are inversely proportional to logarithms of Mg+Mn+Fe (Fig. 4) and (Mg+Mn+Fe)/Fe (Fig. 5), respectively. The contribution of photoelectric effect increases with increasing impurity (Mg, Mn and Fe) concentration for radiation of 0.059MeV (tungsten target X-ray), thus gamma efficiency may decrease with increasing total impurity concentrations (Mg+Mn+Fe). Beta efficiency must be considered together with the Cathodoluminescence (CL) emission. Fe, which works as quencher in CL (Tsukamoto, 1994), may keep radiation energy from beta ray instead of transmitting to activator, thus accumulated dose of calcite may increase with increasing Fe concentration; therefore, beta efficiency may be inversely proportional to logarithm of (Mg+Mn+Fe)/Fe.

Finally, calcite TL dating was applied to understand the timescale necessary for bentonite–alkaline groundwater reaction in a geological framework (Chapter 4). Chronological studies using the TL and U-Th methods on a calcite vein from Luzon, Philippines, have been tried. However, the presence of significant detritus ^{230}Th has hindered the application of U-Th method. The paleodose for the TL was measured with the SARA (single-aliquot regeneration and added dose) method to evaluate the sensitivity change of calcite that occurred through repeated heating of the samples (Buylaert et al., 2006). When the SARA method was not applied, the paleodose was 1.3–3.2 times overestimated for this sample. For the annual dose estimate, we measured the radioactive element concentrations of calcite and the surrounding mafic sample using X-ray fluorescence spectrometry, electron prove micro analyzer, and laser ablation-inductively-mass spectrometry analyses. Alpha, beta and gamma efficiencies were measured, and the age was calculated with the annual dose corrected by these factors. To estimate the annual dose of a heterogeneous sample, detailed three-dimensional distributions of the rock surrounding the samples is necessary. However, because of the small sample size, this information was not preserved. By assuming the ratio of calcite and olivine basalt in annual dose contribution, the calcite age was calculated (Fig. 6). The results indicate that the bentonite had undergone the alteration process for more than 100kyrs.

The results suggest that TL dating method can be applied to calcite, for which other chronological techniques (e.g., the U-Th method) are difficult to apply, provided appropriate corrections considering impurity concentrations Thus TL dating of calcite is useful to provide information for geological and archaeological age determination.

Reference

Aitken, M.J., 1985. Thermoluminescence Dating. Academic Press, London.

Debenham, N.C., Aitken, M.J., 1984. Thermoluminescence dating of stalagmitic calcite. Archaeometry, 26, 2, 155-170.

Buylaert, J.P., Murray, A.S., Huot, S., Vriend, M.G.A., Vandenberghe, D., 2006. A comparison of quartz OSL and isothermal TL measurements on chinese loess. Radiation Protection Dosimetry, Vol. 119, No. 1-4, pp. 474-478.

Davisson, C.M., Evans, R.D., 1952. Gamma-Ray Absorption Coefficients. Reviews of Modern Physics, 24, 2, 79-107.

Flotté, N., Plangnes, V., Sorel, D. and Benedicto, A., 2001. Attempt to date Pleistocene normal faults of the Corinth-Patras Rift (Greece) by U/Th method, and tectonic implications. Geophys. Res. Lett. 28, 3769–3772.

Franklin, A.D., Hornyak, W.F., Tschirgi, A.A., 1988. Thermoluminescence dating of tertiary period calcite. Quaternary Science Reviews, Vol. 7, pp. 361-365.

Kano, A., 2012. Principles and development of the stalagmite paleoclimatology. Journal of the Geological Society of Japan, Vol. 118, No. 3, 157-171.

Medlin, W.L., 1959. Thermoluminescent Properties of Calcite. The journal of chemical physics. Vol. 30 (2), pp. 451-458.

Murray, A.S., Wintle, A.G., 2000. Luminescence dating of quartz using an improved single^aliquot regenerative-dose protocol. Radiation Measurements, 32, 57-73.

Plagnes, V., Causse, C., Fontugne, M., Valladas, H., Chazine, J.H., Fage, L.H., 2003. Cross dating (Th/U-^{14}C) of calcite covering prehistoric paintings in Borneo. Quaternary Research, 60, 172-179.

Roque, C., Guibert, P., Vartanian, E., Bechtel, F., Schvoerer, M., 2001. Thermoluminescence-dating of calcite: study of heated limestone fragments from Upper Paleolithic layers at Combe Sauniѐre, Dordogne, France. Quaternary Science Reviews 20, 935-938.

Suzuki, A., Tanimoto, Y., Kawahata, H., 1999. Coral skeletal records: a reconstruction of palaeoceanographic conditions for the last several centuries. Chikyukagaku (Geochemistry), 33, 23-44.

Townsend, P.D., Luff, B.J., Wood, R.A., 1994. Mn^{2+} transitions in the TL emission spectra of calcite. Radiation Measurement, Vol. 23, Nos 2/3, pp. 433-440.

Tsukamoto, H., 1994. Geological application of luminescent microscopy and spectroscopy. Chishitsu News, 474, 46-56.

Watanabe, Y., Nakai, S., Lin, A., 2008. Attempt to determine U-Th ages of calcite veins in the Nojima fault zone, Japan. Geochemical Journal, Vol. 42, pp. 507-513.

Wefer, G., Berger, W.H., 1991. Isotope paleontology: growth and composition of extant calcareous. Marine Geology, 100, 207-248.

Zimmerman, D.W., 1972. Relative thermoluminescence effects of alpha- and beta-radiation. Radiation effects, Vol. 14, pp. 81-92.

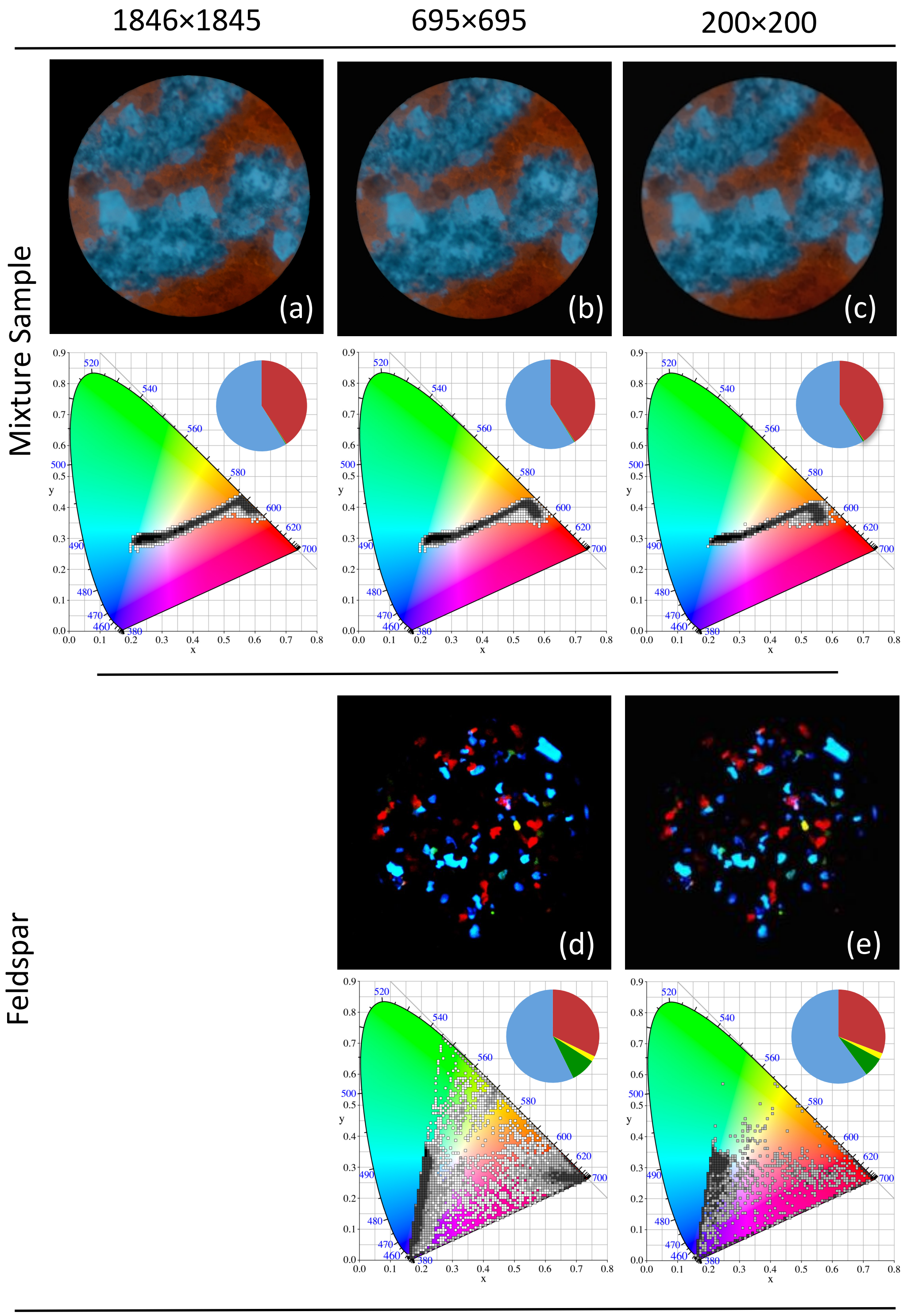

Fig. 1 Results of TLCI analysis using a Java application for the mixture sample (quartz and calcite) and feldspar. For mixture sample, file size is (a) 1846×1845, (b) 695×695 and (c) 200×200. For feldspar, (d) 695×695 and (e) 200×200. Circles show the proportion of each color.

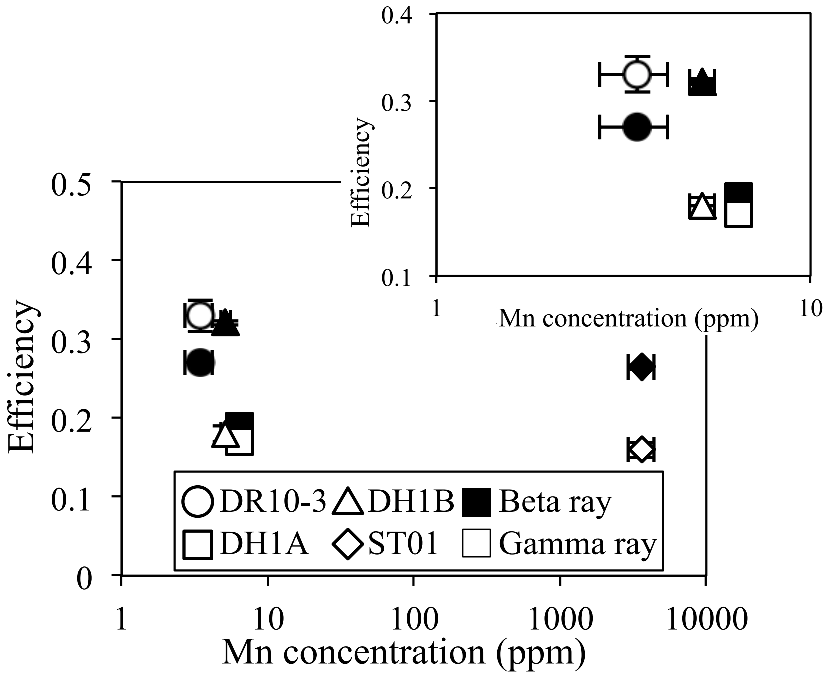

Fig. 2 Plot of beta and gamma efficiencies as a function of Mn concentration. Small figure in the upper right corner is enlarged views.

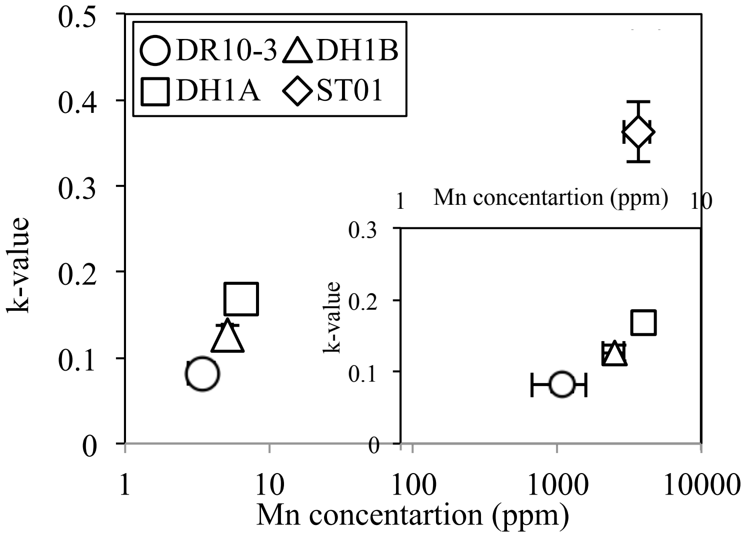

Fig. 3 Plot of k-value as a function of Mn concentration. Small figure in the lower right corner is enlarged views.

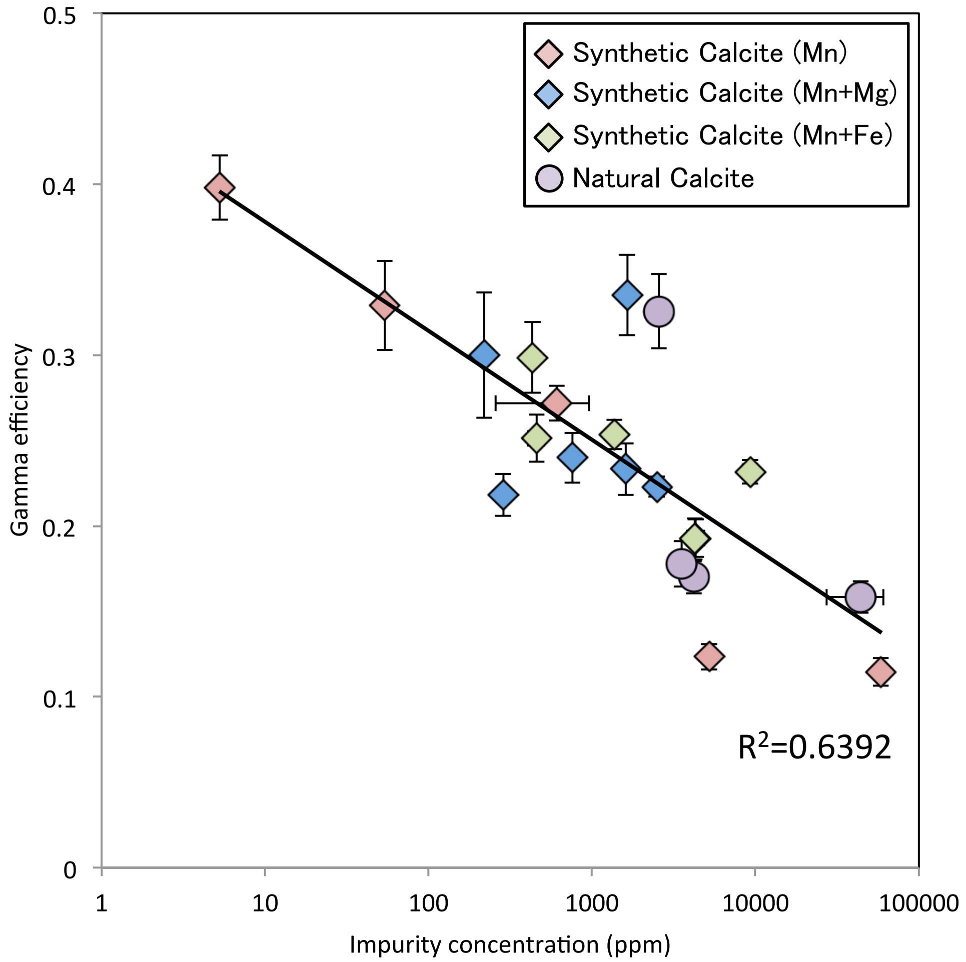

Fig. 4 Plot of gamma efficiency as a function of impurity concentrations. Impurity concentrations are Mn, Mg+Mn, Fe+Mn, and Mg+Fe+Mn concentrations for Synthetic calcite (Mn), Synthetic calcite (Mn+Mg), Synthetic calcite (Mn+Fe) and Natural calcite, respectively.

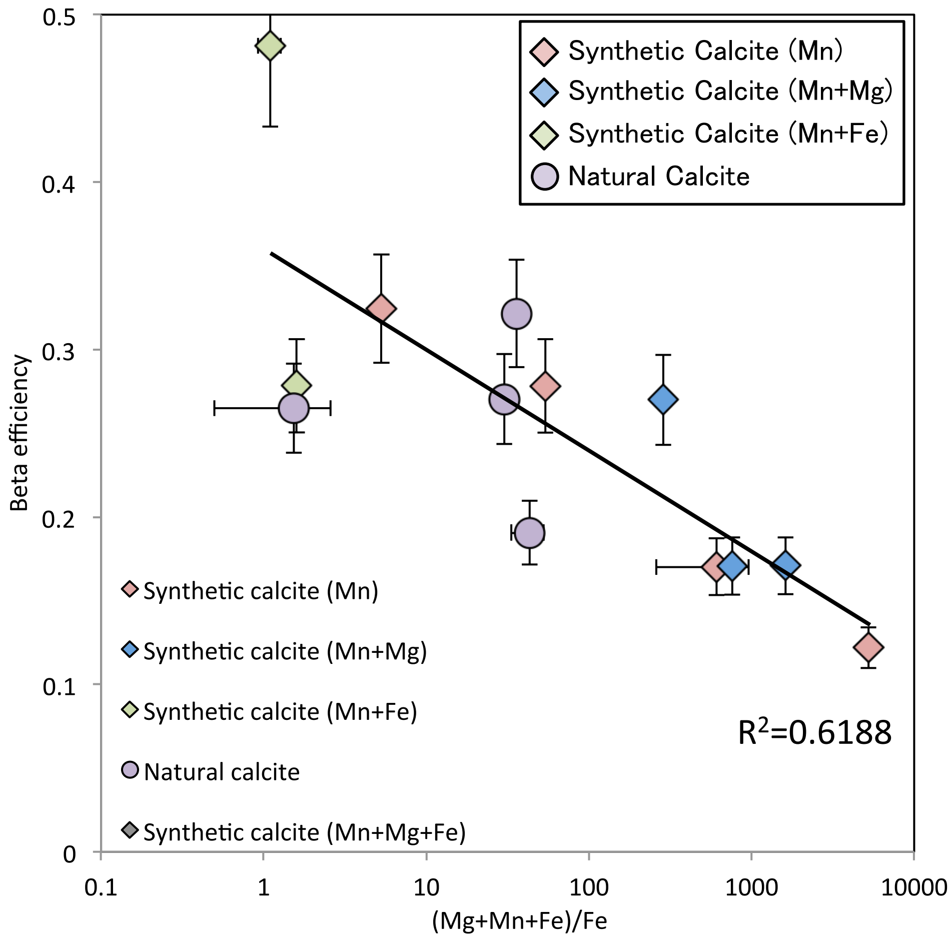

Fig. 5 Plot of beta efficiency as a function of (Mg+Mn+Fe)/Fe. (Mg+Mn+Fe)/Fe are Mn, Mg+Mn, (Mn +Fe)/Fe, and (Mg+Mn+Fe)/Fe for Synthetic calcite (Mn), Synthetic calcite (Mn+Mg), Synthetic calcite (Mn+Fe) and Natural calcite, respectively.

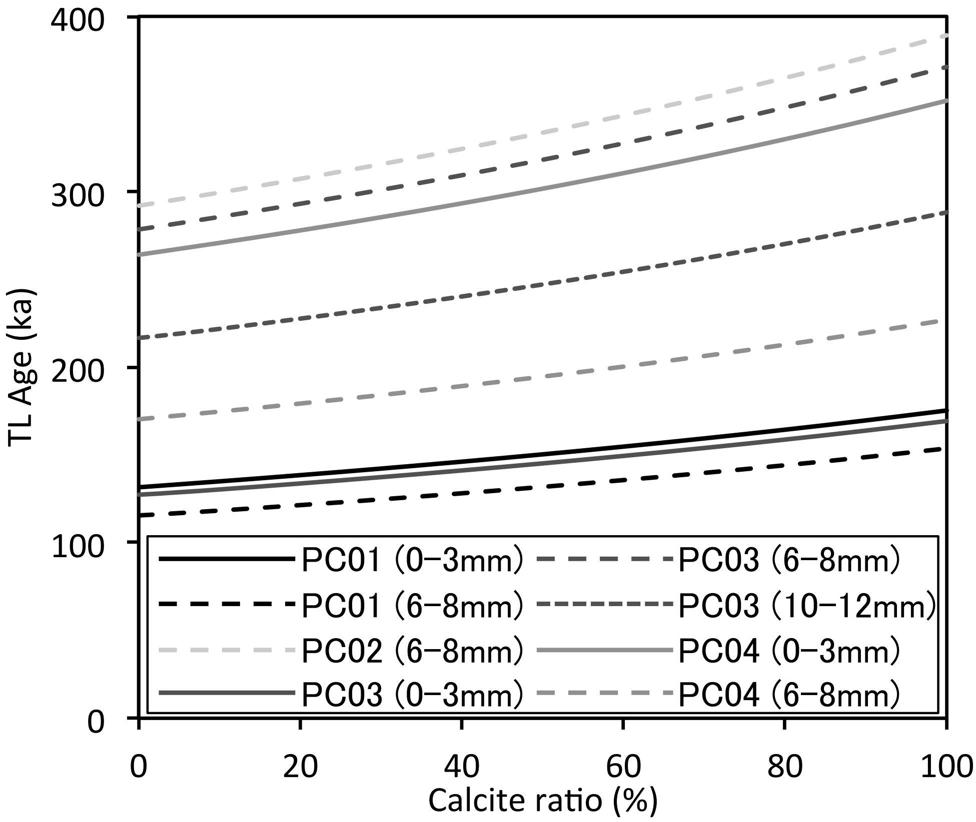

Fig. 6 Results of TL dating of calcite vein from Luzon, Philippines, assuming the ratio of annual dose contributions from the calcite and the olivine basalt.

平成29年 2月3 日

学位論文審査報告書（甲）

1．学位論文題目（外国語の場合は和訳を付けること。）

Thermoluminescence characteristics of calcite for precise age determination

(方解石の熱ルミネッセンス特性研究と正確な年代測定への応用)

2．論文提出者 (1) 所　属　自然システム学　専攻

(2) 氏　名　小形　学（おがた　まなぶ）

3．審査結果の要旨（600～650字）

本学位論文では，地球環境変動研究，災害史研究，考古学的研究に不可欠な年代決定を，さまざまな環境下で普遍的に存在する方解石をもちいて実施することを可能するため，方解石に適用可能な熱ルミネッセンス年代測定に目を付け，基礎実験を行うとともに，フィリピンの方解石脈の年代測定を例として行ったものである。基礎実験では方解石の微量化学組成の違いと各種放射線によるルミネッセンス発生の効率について，天然方解石のみでなく，化学組成をコントロールした合成方解石を作成することによって研究を行っている。

これまでの既存の研究では方解石の化学組成と発光曲線の形状を吟味するものが主体であり，実際の年代の評価に必要な定量的な蓄積放射線量の見積もりにおける化学組成の寄与や放射線種の違いによるルミネッセンス発生の効率の吟味は新しい取組みである。実際の天然試料の年代測定の取り組み結果からも明らかにされたように方解石年代学に新たな扉を開いた。また研究成果の一部は公表されており，かつ副論文や現在投稿・審査中の論文があることから，本審査委員会は全会一致で学位の申請にふさわしい研究であると判断した。

4．審査結果　(1) 判　定（いずれかに○印）　合　格　・　不合格

(2) 授与学位　博　士（理学）